

DFT with SIESTA, Data Visualization, and a Sophomore-level CURE with the MIT Atomic-Scale Modeling Toolkit



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nanoHUB webinar

PHYS 10: Introductory Physics III aka Modern Physics (fall 2022, fall 2023)

- Sophomore-level class for around 20 students, all undergraduate physics majors
- Gentle introduction to quantum mechanics in preparation for later more intensive course
- Gateway from large introductory classes with mostly engineering students, to small upper-division classes
- Introduces more intensive lab exercises, with lab reports

Topics: Schrödinger equation, particle in a box, scattering from step potentials, atomic structure, nuclear structure, Bose-Einstein and Fermi-Dirac distributions, particle/wave duality

Goals:

- Improve learning of introductory of quantum mechanics by showing application to condensed matter physics
- Demonstrate use of computation in physics research
- Promote retention of students in physics by helping them feel like physicists

Course-based Undergraduate Research Experience (CURE)

Bringing the excitement of research into the classroom!

Key aspects are: students learning and using research methods, having input into the project, generating new research data, and analyzing it to draw conclusions that are not known beforehand – in contrast to ‘cookbook’ / verification-style labs.

Many studies show:

- Improves learning and motivation, promotes independent thinking, and increases retention of students in the major and STEM
- Students apply knowledge, get a taste of research, feel like a scientist, have sense of belonging, go on to more intensive research projects
- Especially beneficial for minoritized/underrepresented students

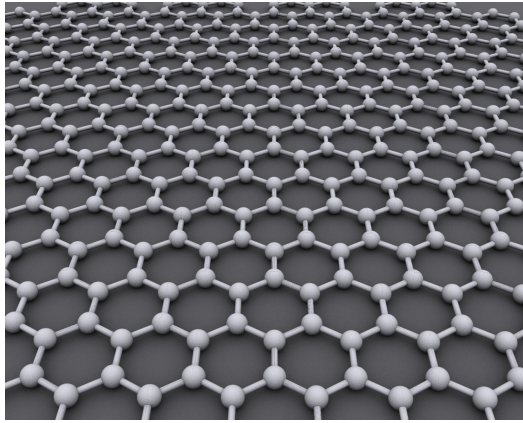
D. Lopatto, *Science in Solution: The Impact of Undergraduate Research on Student Learning*, Research Corporation for Science Advancement (2009). https://www.researchgate.net/publication/229078320_Science_in_Solution

Rory Waterman and Jen Heemstra, eds. *Expanding the CURE Model: Course-Based Undergraduate Research Experience*, Research Corporation for Science Advancement (2018).

<https://rescorp.org/gdresources/publications/Expanding-the-CURE-Model.pdf>

Use computation in condensed matter: cheap, well-defined, reproducible,
and **easy to get to the frontiers of knowledge.**

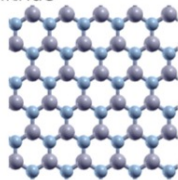
2D materials: atomically thin crystals, periodic in 2D



graphene: the original

Nobel Prize in Physics 2010, Geim and Novoselov
Large sheets of carbon, just one atom thick

Boron nitride

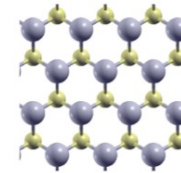


also one atom thick

may be a few atoms thick also

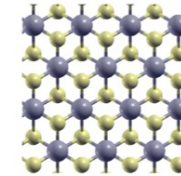
transition-metal dichalcogenides (TMDCs)

TMDCs-trigonal prismatic



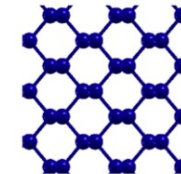
e.g. 1H-MoS₂

TMDCs-octahedral



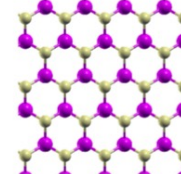
e.g. 1T-MoS₂

Phosphorene and IV-VI



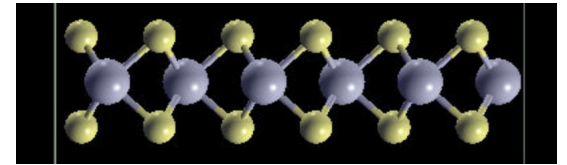
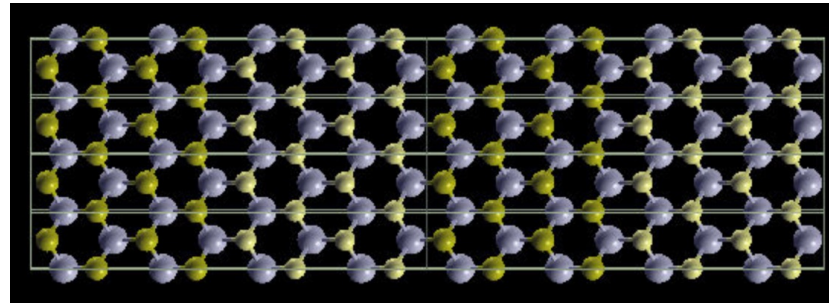
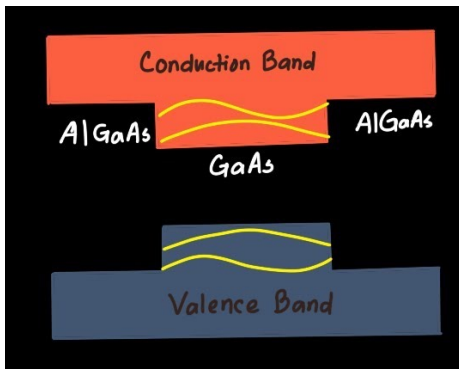
e.g. black phosphorus,
SnS

Group III chalcogenides



e.g. GaSe

Your research mission: quantum well structures in 2D materials



How could we design new quantum well structures? Need two materials with similar structures.

e.g. MoS_2 , MoSe_2 , WS_2 , WTe_2 , etc.

To see if they would work: calculate the wavefunctions, for a given pair.

See if the wavefunction are *confined* in one material, like in square well model.

This is a research question – we don't know the answer yet! Hopefully we will find something interesting, and maybe the most interesting structures can be made in the lab.

nanoHUB and the MIT Atomic-Scale Modeling Toolkit

NSF-funded project since early 2000s, headquartered at Purdue University

GUIs for simulations, course resources, webinars, forums. Computation is done remotely on their clusters.

https://nanohub.org/tools/ucb_compnano/

Begun for graduate Computational Nanoscience class at UC Berkeley in 2007, developed originally by Elif Ertekin (now at UIUC) and Jeffrey Grossman (now at MIT), a bit by Lucas Wagner (UIUC, here at ES23 also)

I was TA and developer for class in 2009.

I am main developer at UC Merced since 2016, with Enrique Guerrero (now at Cal Poly Humboldt).

Design philosophy: manage complexity of underlying code, less is more

No need for: SSH, Bash, Fortran, make, SLURM, emacs, gnuplot, Python, etc.

Component tools

Averages and Error Bars

Molecular Dynamics (Lennard-Jones)

Molecular Dynamics (Carbon Nanostructures and More)

Monte Carlo (Hard Sphere)

Monte Carlo (Ising Model)

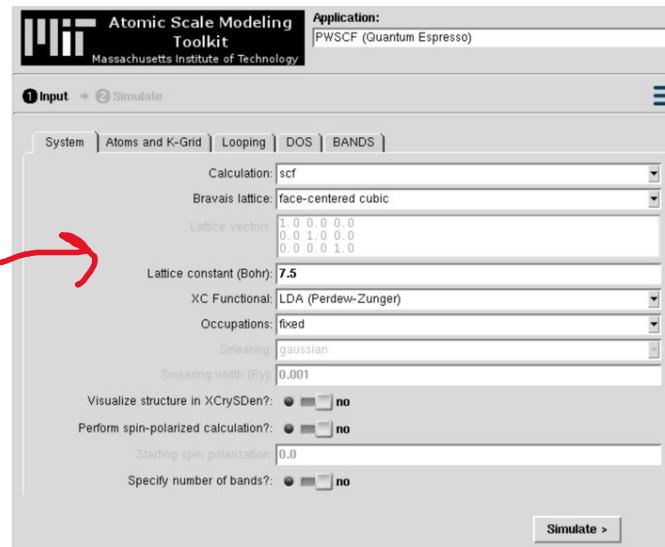
Quantum Chemistry (GAMESS)

DFT for Solids and 2D Materials (Quantum Espresso)

Crystalline Structures and Densities (XCrySDen)

DFT for Solids, Surfaces, and Molecules (SIESTA)

Quantum Monte Carlo (QWalk)



The screenshot shows the 'Input' tab of the MIT Atomic Scale Modeling Toolkit. The 'Application' dropdown is set to 'PWSCF (Quantum Espresso)'. The 'System' tab is selected, showing parameters for a face-centered cubic lattice with a lattice constant of 7.5 Bohr. The 'Calculation' is set to 'scf'. A red arrow points from the 'DFT for Solids and 2D Materials (Quantum Espresso)' component in the list to the 'Calculation' dropdown.

Application: PWSCF (Quantum Espresso)

1 Input 2 Simulate

System | Atoms and K-Grid | Looping | DOS | BANDS

Calculation: scf

Bravais lattice: face-centered cubic

Lattice vectors: 1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 1 0

Lattice constant (Bohr): 7.5

XC Functional: LDA (Pardew-Zunger)

Occupations: fixed

Smearing: gaussian

Smearing width (Ry): 0.001

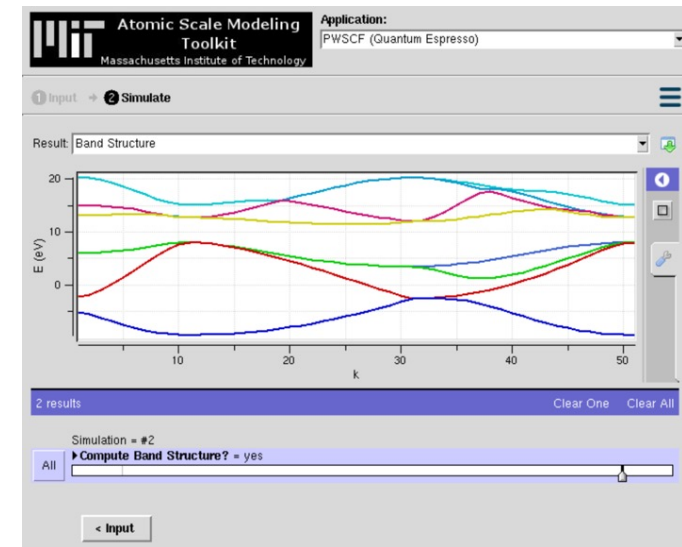
Visualize structure in XCrySDen?: ☐ no

Perform spin-polarized calculation?: ☐ no

Starting spin polarization: 0.0

Specify number of bands?: ☐ no

Simulate >

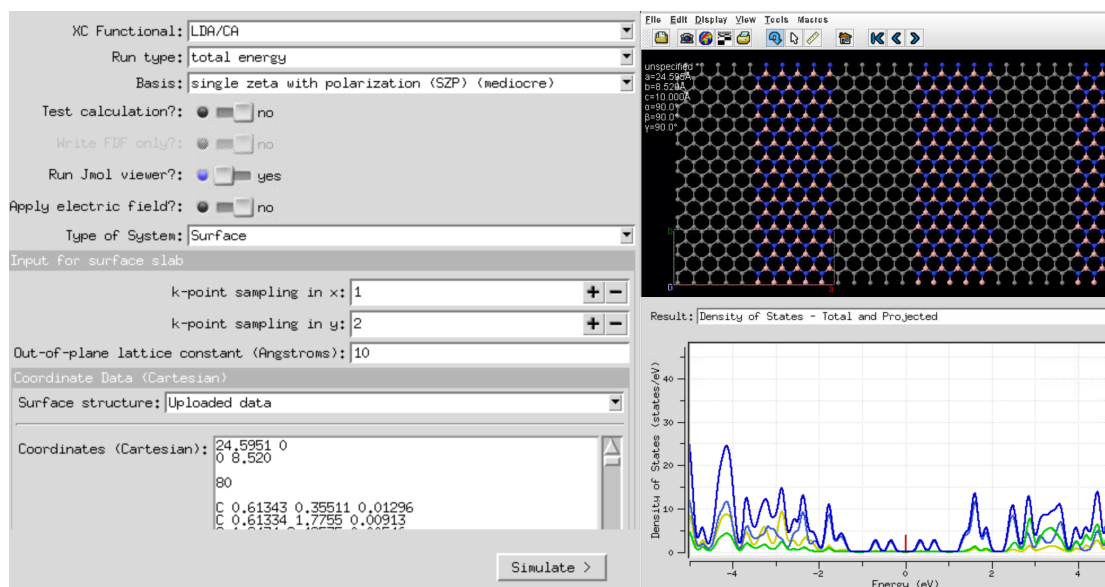


SIESTA interface

SIESTA: Spanish Initiative for the Electronic Simulation of Thousands of Atoms
numerically defined local orbital DFT code

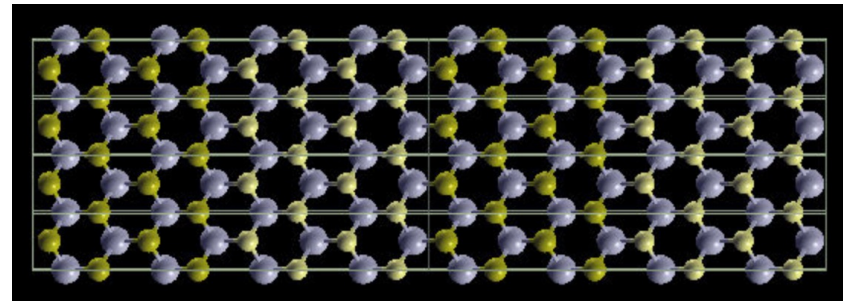
Alberto García *et al.*, *J. Chem. Phys.* 152, 204108 (2020)

<https://departments.icmab.es/leem/siesta/>

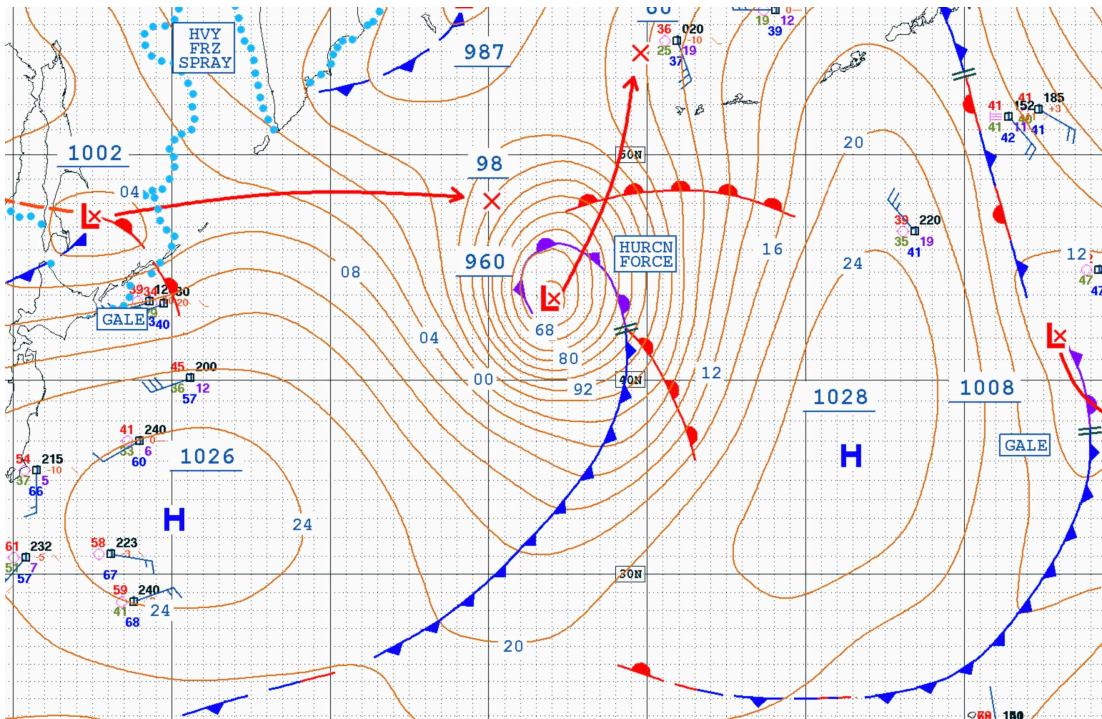


CURE on heterojunctions

- Guest lecture in class: condensed matter physics, 2D materials, quantum dots, isosurfaces, envelope functions, research question
 - One of 7 lab exercises in the semester, 6 hour session
1. Warm-up on square wells and envelope functions
 2. Analyze isosurfaces of H atom calculation (familiar 1s, 2s, 2p wavefunctions)
 3. Common benchmark calculation: MoS_2 / MoTe_2 system, fixed coordinates. Analyze effective potential, density, wavefunctions.
 4. Novel calculation with lab partner: assigned pair chosen from MoO_2 , MoS_2 , MoSe_2 , MoTe_2 , WO_2 , WS_2 , WSe_2 , WTe_2 . Find relaxed coordinates, then analyze potential, density, wavefunctions in defined protocol.
 5. Look for something else interesting in the calculation results (e.g. structural changes, band structure, etc.)



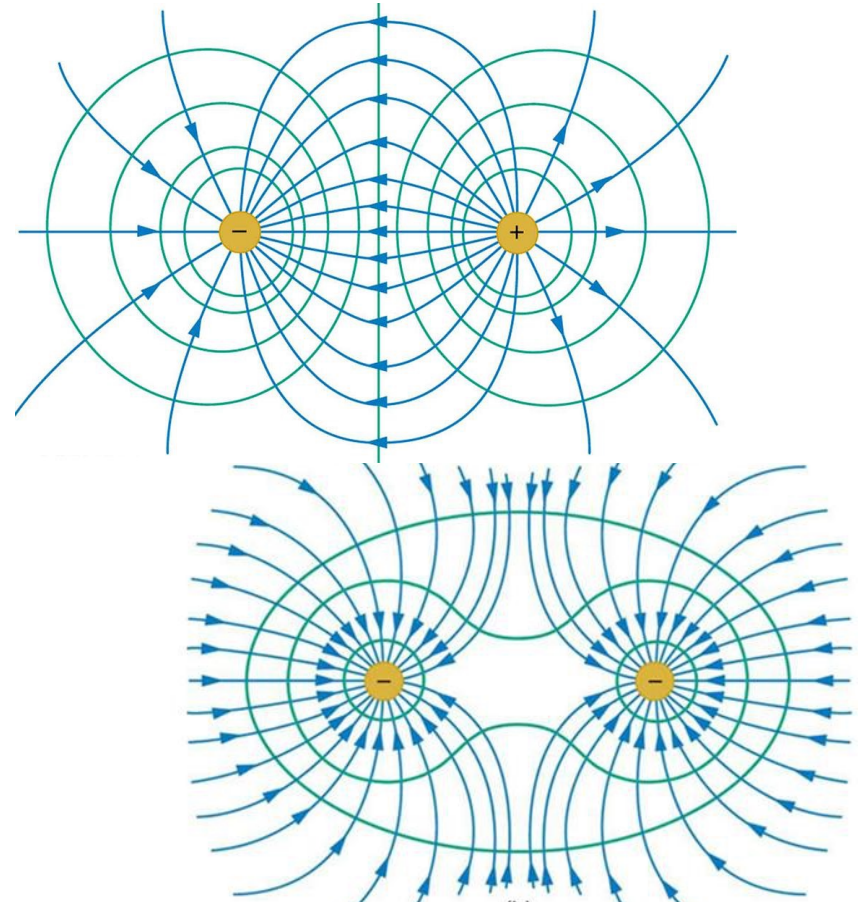
Visualization concept: isosurfaces, or in 2D isolines (contours)



weather map (isobars), values in mmHg

https://www.eoas.ubc.ca/courses/atasc113/sailing/met_concepts/11-met-marine-weather/11c-forecasting/

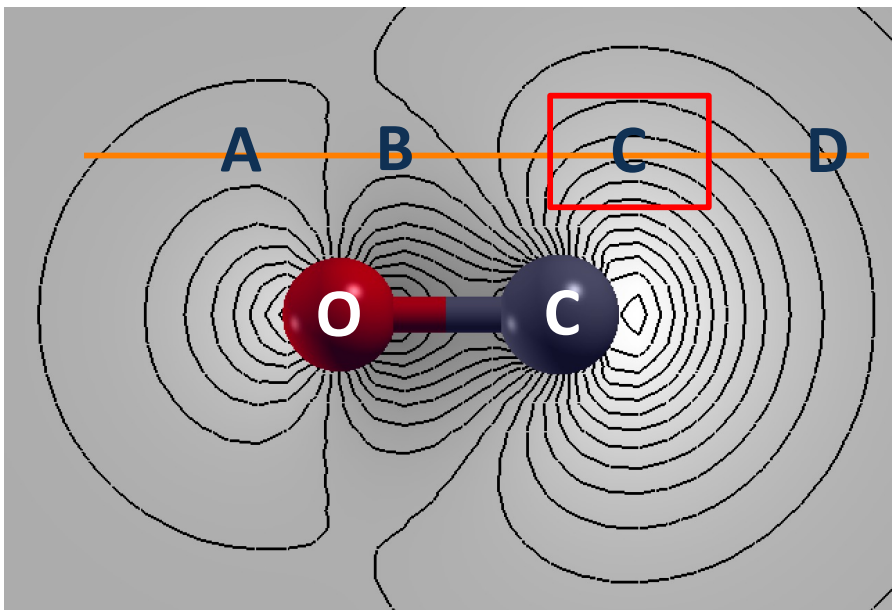
Definition phrased mathematically: $\{\vec{r} \mid f(\vec{r}) = f_0\}$



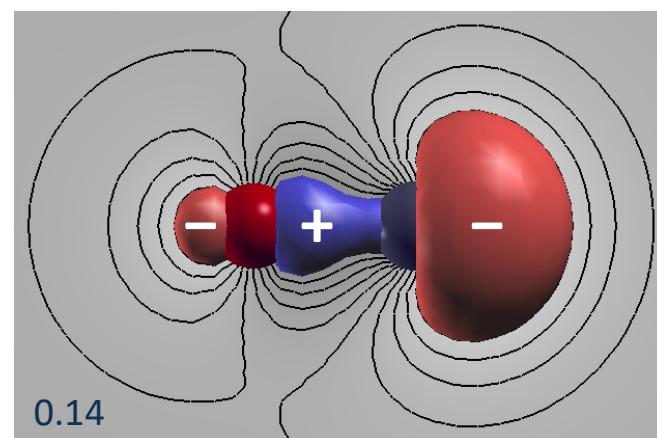
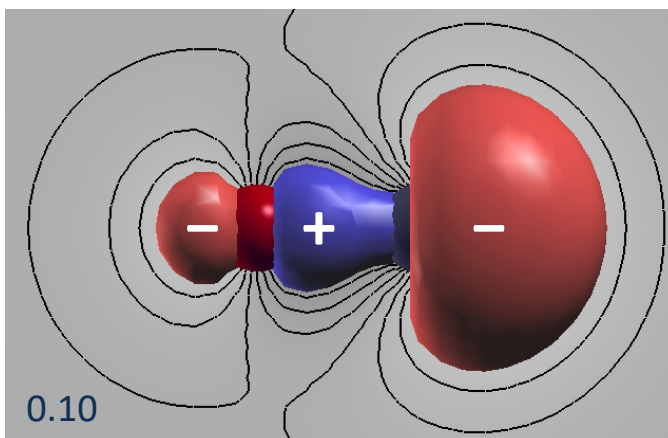
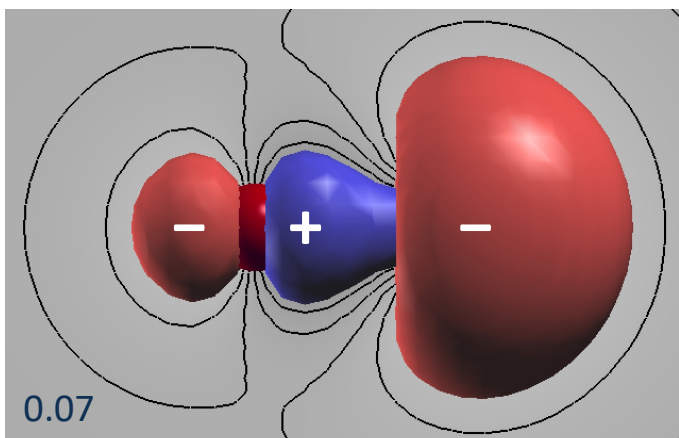
Equipotential lines for electrostatics

<https://texasgateway.org/resource/24-equipotential-lines>

Question: which point has the largest absolute value of the wavefunction?



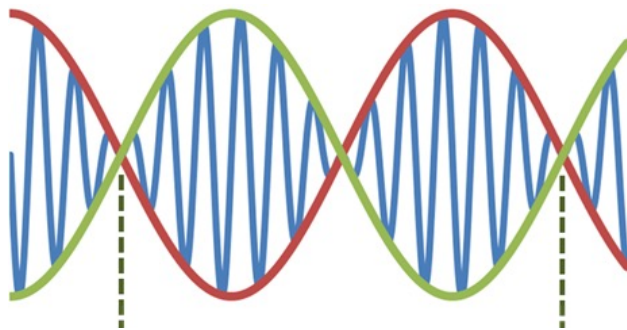
Wavefunction of carbon
monoxide (CO) molecule



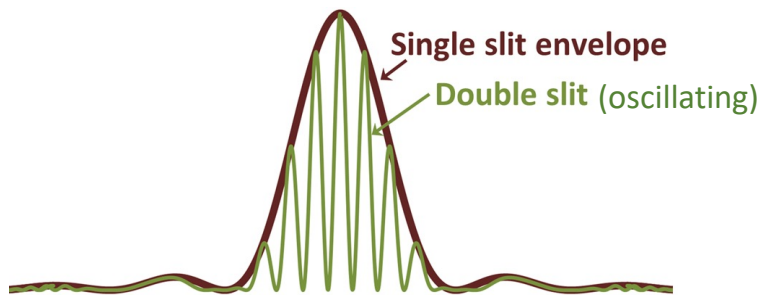
Math/physics concept: envelope function

Express a function with a complicated shape as product of a smooth envelope function and a rapidly oscillating function

$$\psi(x) \approx \Psi_{\text{envelope}}(x) \Psi_{\text{oscillating}}(x)$$



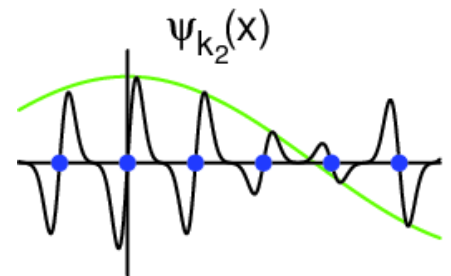
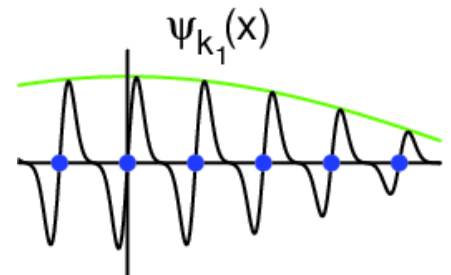
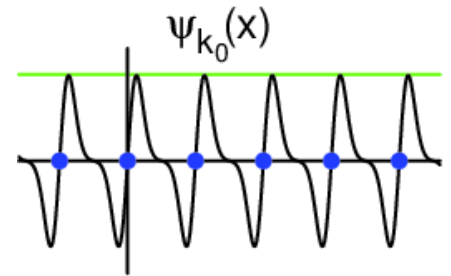
envelope
oscillating



Single slit envelope

Double slit (oscillating)

https://en.wikipedia.org/wiki/Envelope_%28waves%29



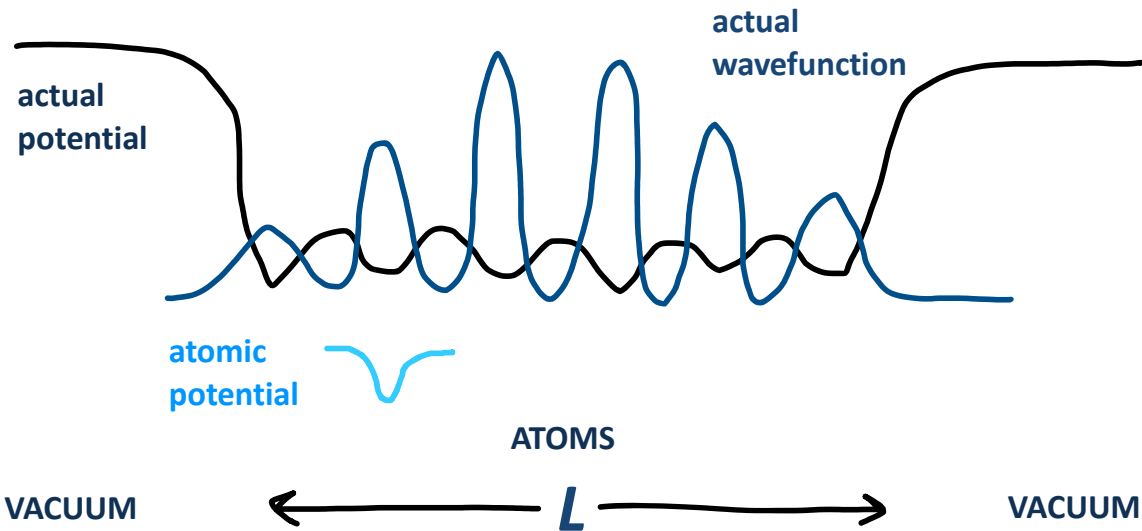
Sometimes, the rapidly oscillating function is a sum of equally spaced pieces.

A. Mostofi *et al.*, *Rev. Mod. Phys.* 84, 1419 (2012)

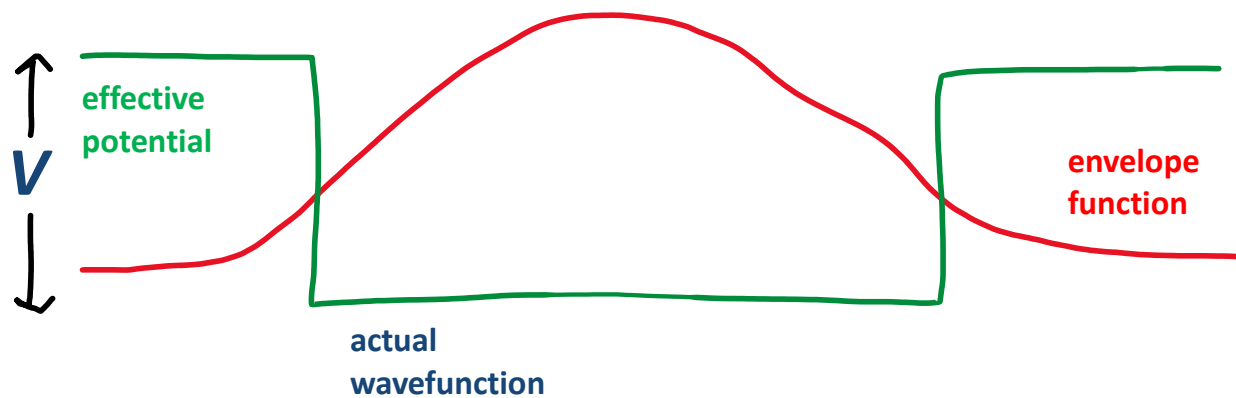
$$\psi(x) \approx \Psi_{\text{envelope}}(x) \sum_n \phi(x - na)$$

From the square well model to quantum dots

Could we actually make a square potential out of atoms?



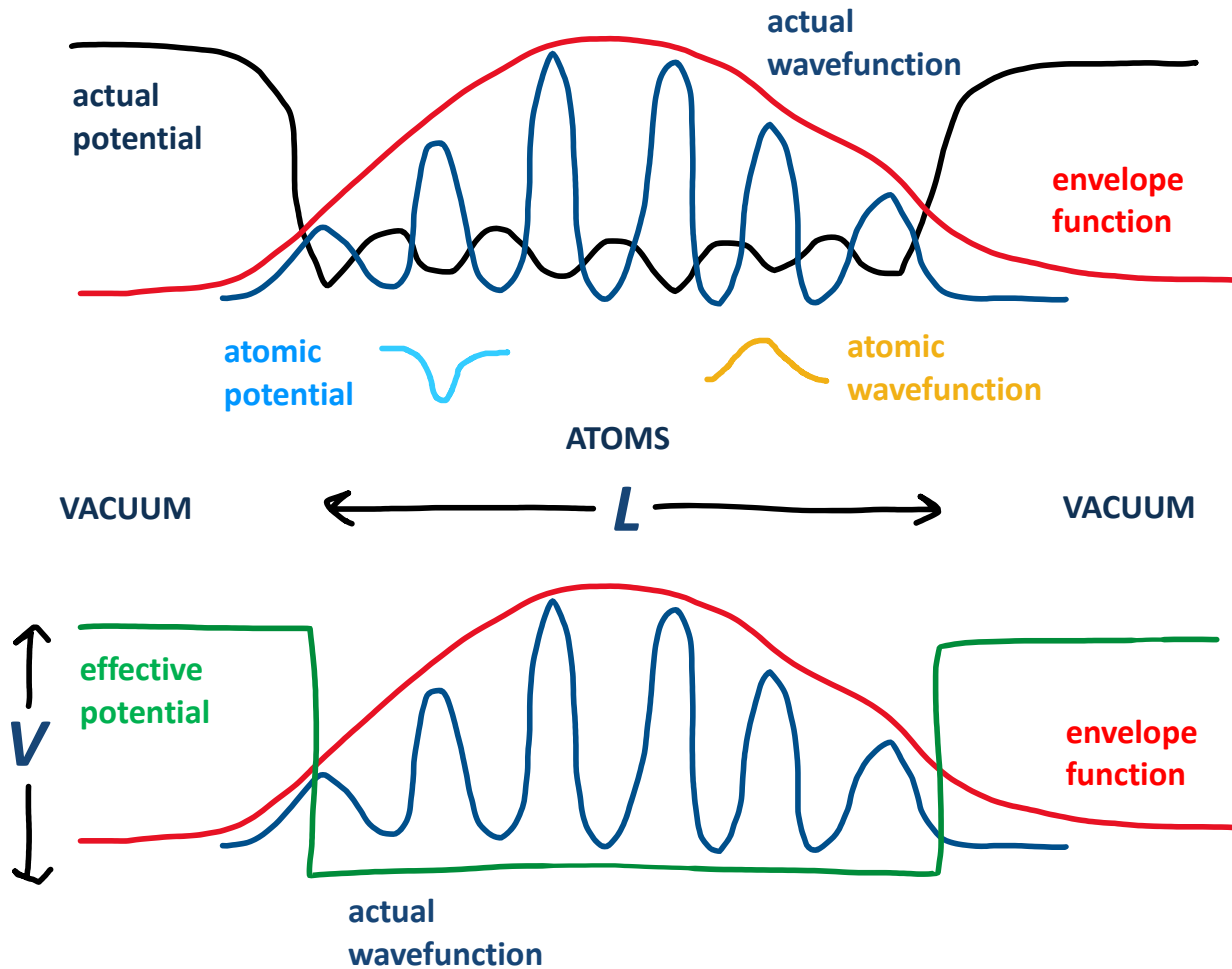
Wiggly potential and wavefunction



Smooth potential and wavefunction

From the square well model to quantum dots

Could we actually make a square potential out of atoms?



Wiggly potential and wavefunction

True electron mass, m_e

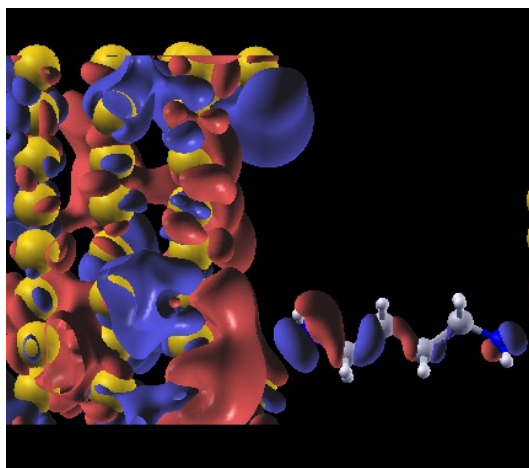
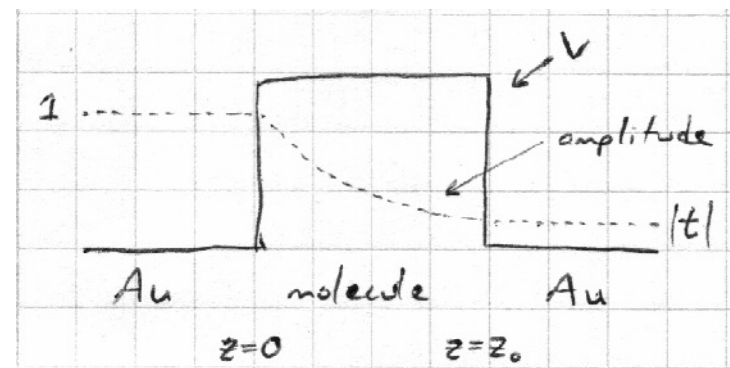
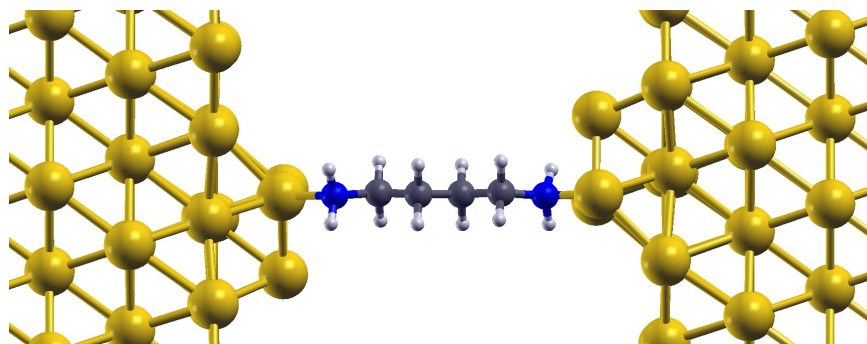
Smooth potential and wavefunction

Effective mass, $m^* \sim 0.1 m_e$

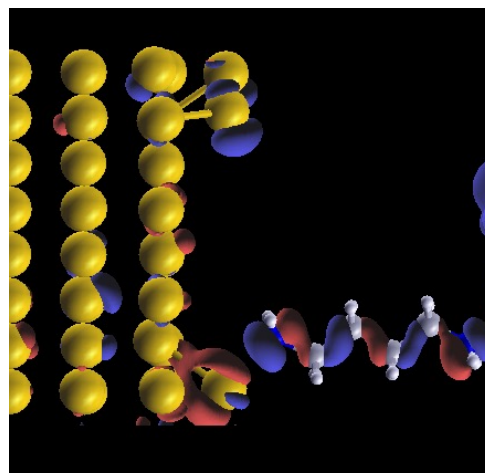
$$E_n = \frac{n^2 \hbar^2 \pi^2}{2m^* L^2}$$

(for infinite potential depth)

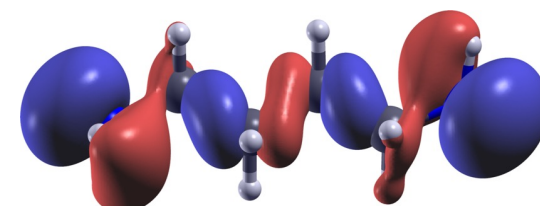
An example: a molecule between pieces of gold, “molecular electronics”



exponentially decaying wiggly wavefunction



wiggly wavefunction divided by exponential decay



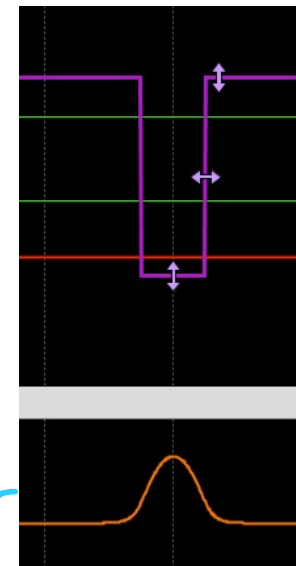
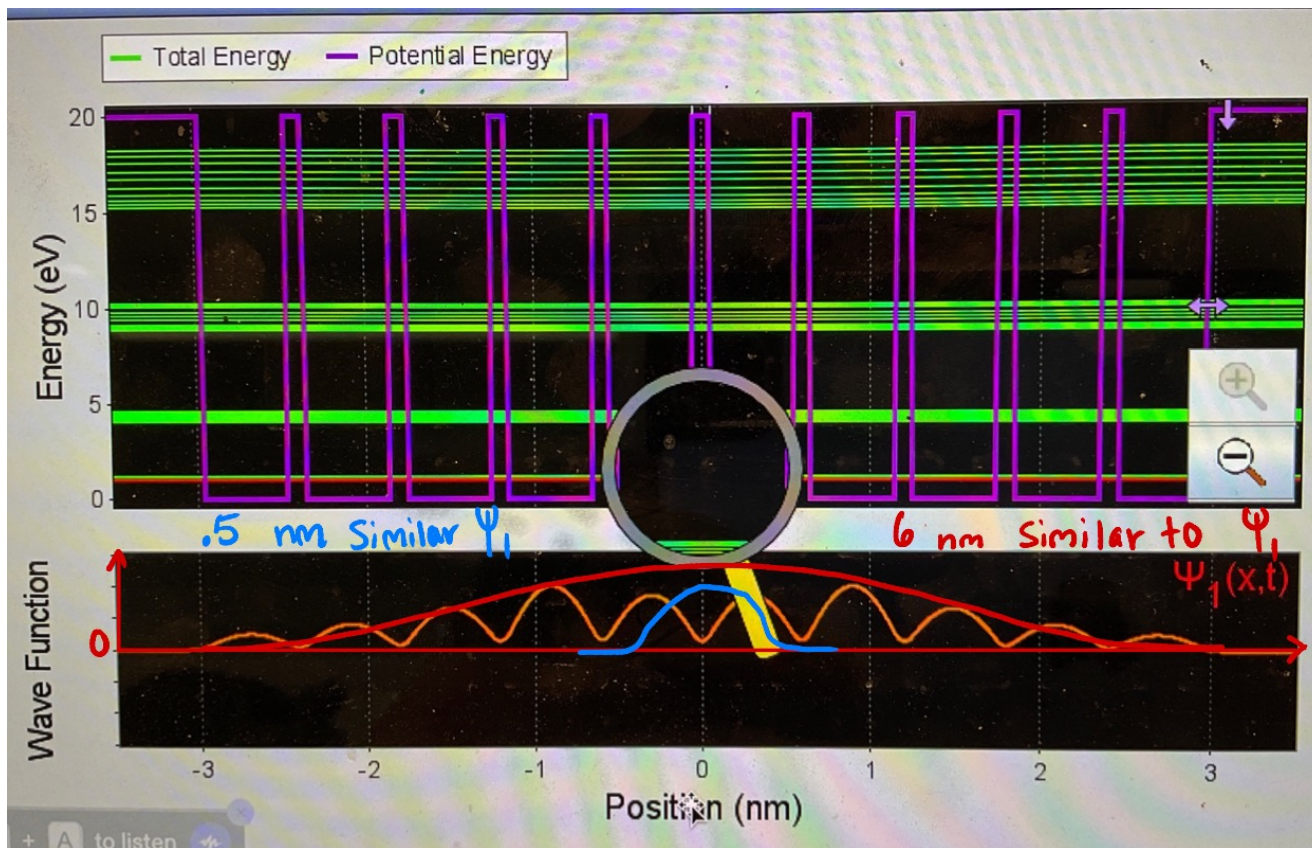
wavefunction of
molecule by itself

source: my PhD thesis, 2012

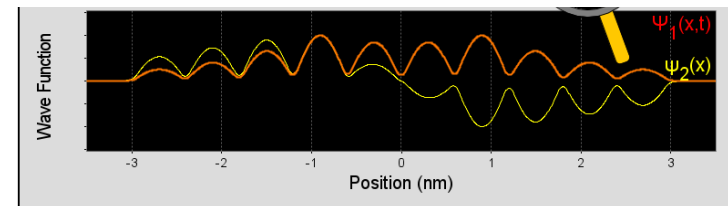
Warm up: envelope functions in a system of square wells

PhET Quantum Bound States exercise:

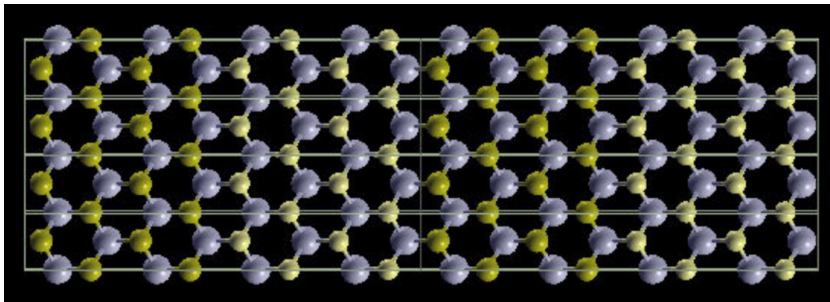
<https://phet.colorado.edu/sims/cheerpj/bound-states>



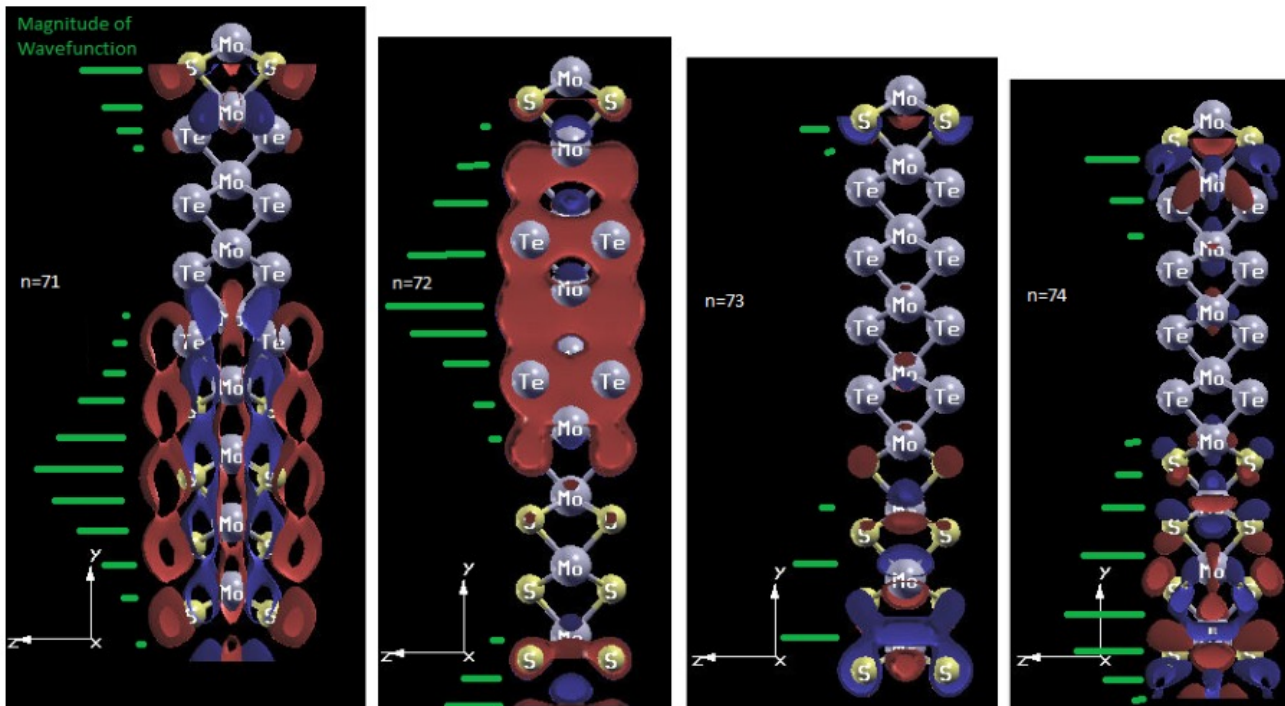
same here
(few got this)



Common benchmark calculation: MoS_2 / MoTe_2 system



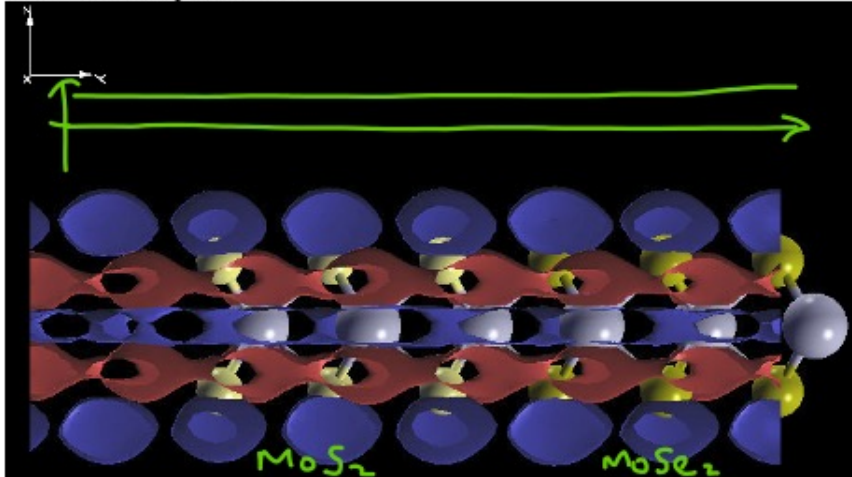
structure



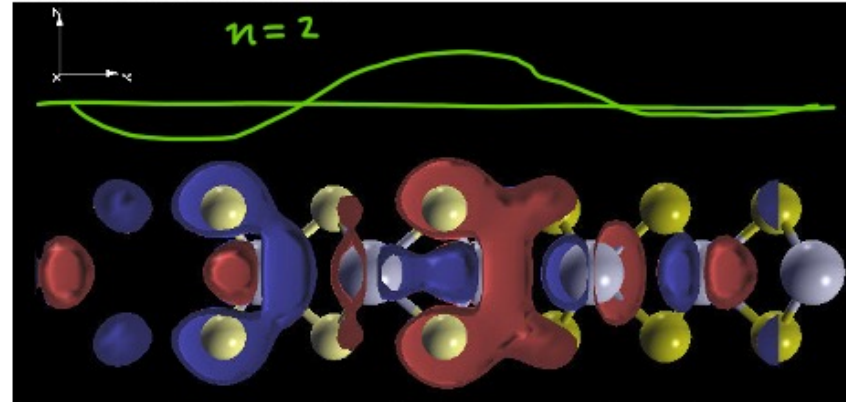
wavefunctions around
Fermi energy, with sketch
of envelope functions

Some of my sketches from a solution in the 2022 edition

Wavefunction 54: isovalue 0.03
Uniform envelope function



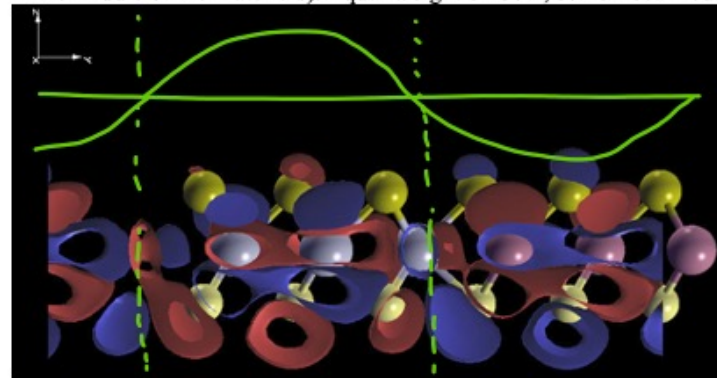
Wavefunction 56: isovalue 0.04



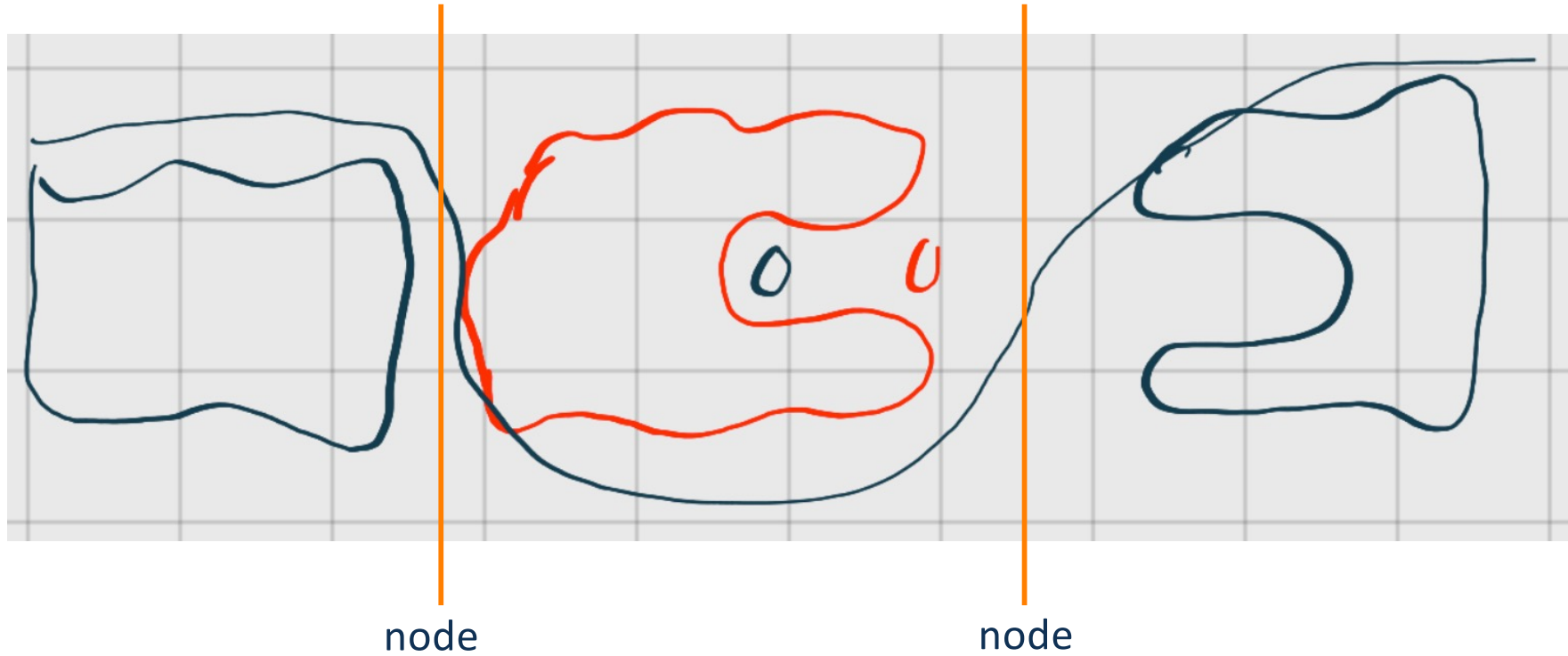
The wavefunction has one node, in the MoS₂ region, and is much smaller in the MoSe₂ region, showing confinement and quantum well-type behavior.

Wavefunction 53, isovalue 0.03.

Two nodes, at boundaries between materials (unlike #53 of MoS₂/MoSe₂ where the nodes were in the middle of the materials). Equal weight on both, so not localized.



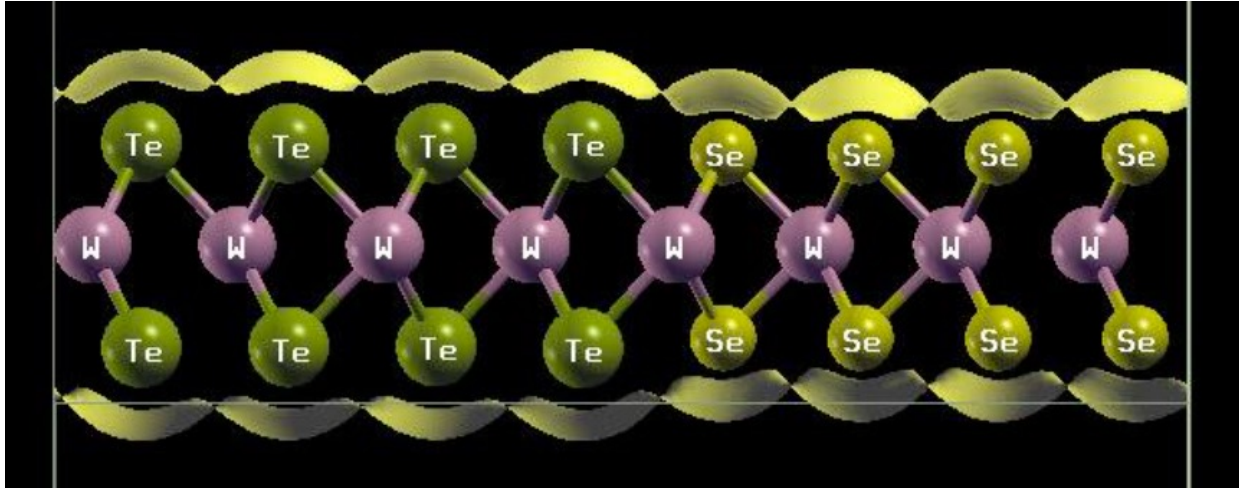
Example calculation: $\text{WTe}_2 / \text{WSe}_2$ system



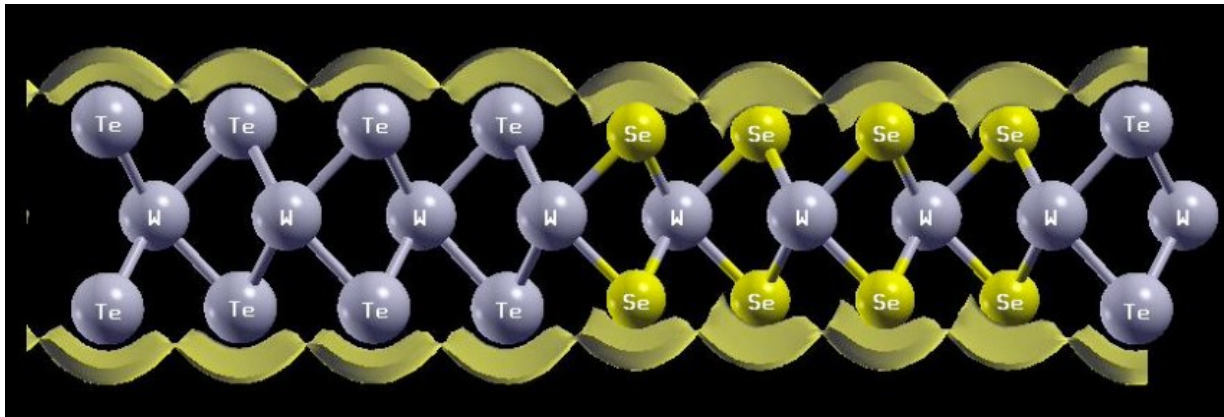
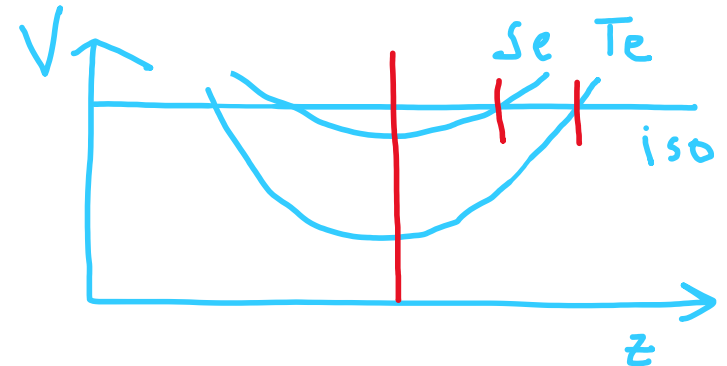
sketched wavefunction, labeled as “no nodes”

more effort on explanation of nodes, and practice with square well, needed

Example calculation: $\text{WTe}_2 / \text{WSe}_2$ system



Kohn-Sham **potential**:
deeper in Te than Se.
(a bit complicated to reason)

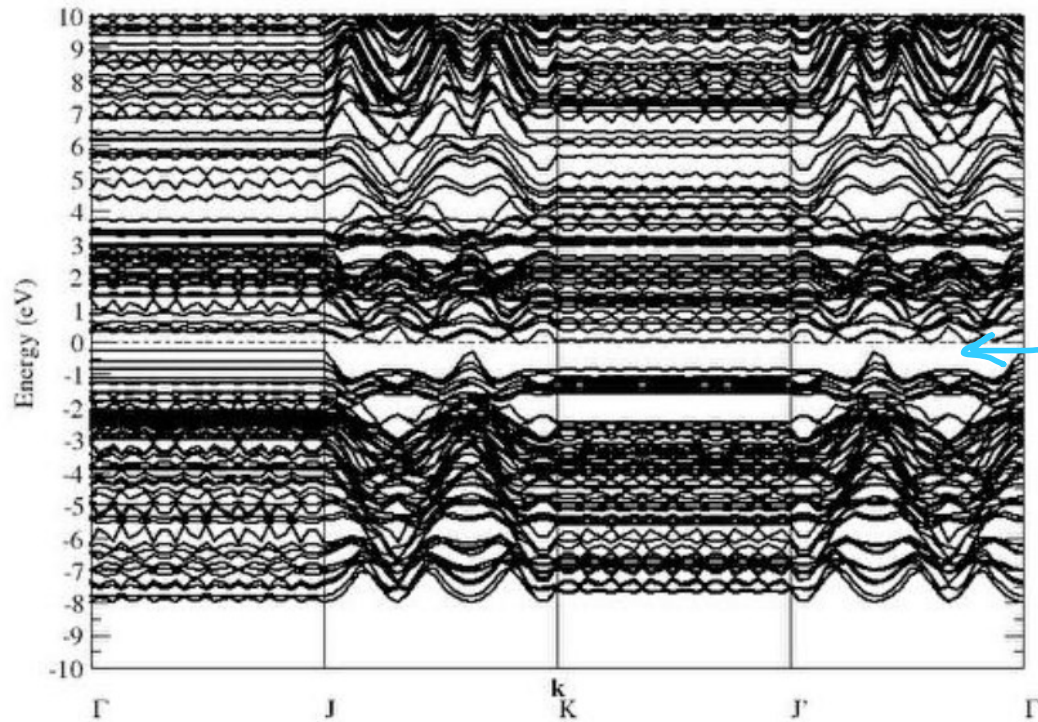


density: more on Te than Se

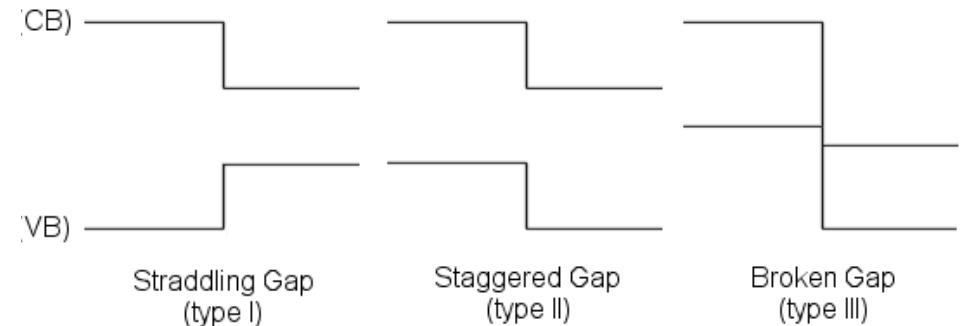
Se being more electronegative
does not offer a simple
explanation

Exploring some other features: bandstructure

Band Structure Plot



- Many looked at this.
- Not something they had learned about.
- Not necessarily accurate with PBE.
- Gap can be reduced or disappear.



Improvements from 2022 to 2023

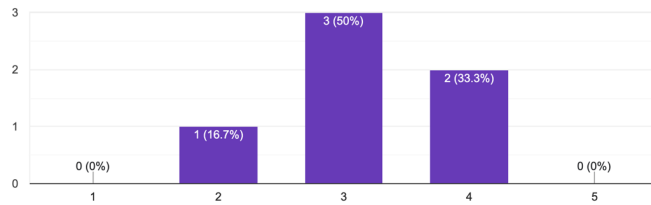
- Revised square well exercise: better alignment to introducing envelope functions
- Better choice of benchmark calculation that shows confinement more clearly
- Improved interface for visualizing wavefunctions, less confusing
- Alternating strips of material are 4 unit cells wide, not 3 unit cells, showing confinement more clearly

Plans for future

- Improved explanation of envelope functions as applied to square well system: consideration of spatial location of nodes is essential to understand $n=1$ vs $n=2$ cases
- Improved plotting of bandstructure
- Improved plotting of wavefunctions, density, potential regarding alignment with atomic structure
- Better explanation of idea of open-ended parts of lab
- Trying other 2D material heterojunctions

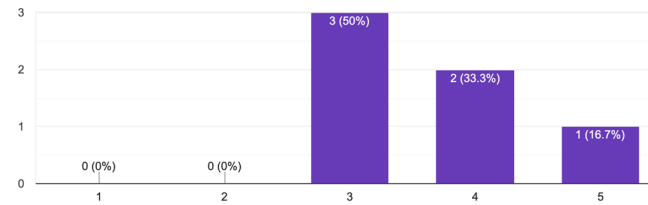
Student feedback in post-survey

How difficult did you find this lab compared to other PHYS 010 labs?
6 responses



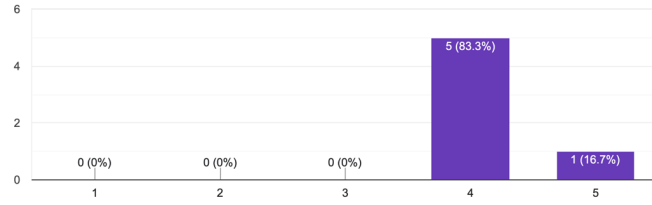
1 = much less, 5 = much more

To what extent did doing this lab increase your interest in physics research?
6 responses



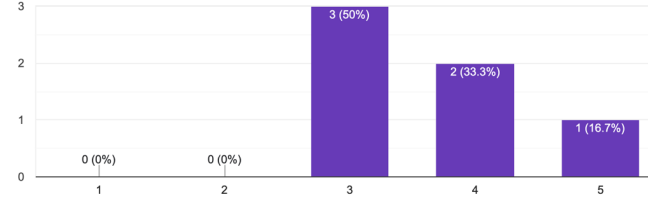
1 = not much, 5 = a great deal

How interesting did you find this lab compared to other PHYS 010 labs?
6 responses



1 = not much, 5 = a great deal

To what extent did doing this lab increase your interest in physics in general?
6 responses



1 = not much, 5 = a great deal

What part of this lab did you find **most interesting**?

“The fact that I had no real idea of what the results would be.”

“This lab increased my levels of interest in physics research, because I really liked the programming aspect of research and creating models on the computer. The programming helped me visualize the materials which I thought were really cool to look at.”

Conclusions

- nanoHUB GUI allows focus on quantum physics not computational methods
- Real calculations can be accessible for sophomores
- Students were enthusiastic about exploratory lab exercises
- Use nanoHUB and/or my CURE ideas in your courses!

Acknowledgments

Students in PHYS 10, fall 2022 and fall 2023

Elsa Vazquez and Dr. Rafael Del Grande, co-facilitators of lab activity

Course instructors Kinjal Dasbiswas and Dustin Klecker, TAs Subhaya Bose and Kevin Collins

Technical support from nanoHUB team (especially Steven Clark)

Funding from NSF CAREER award DMR-2144317



Visualizing crystal structures and Wigner-Seitz cells in XCrySDen

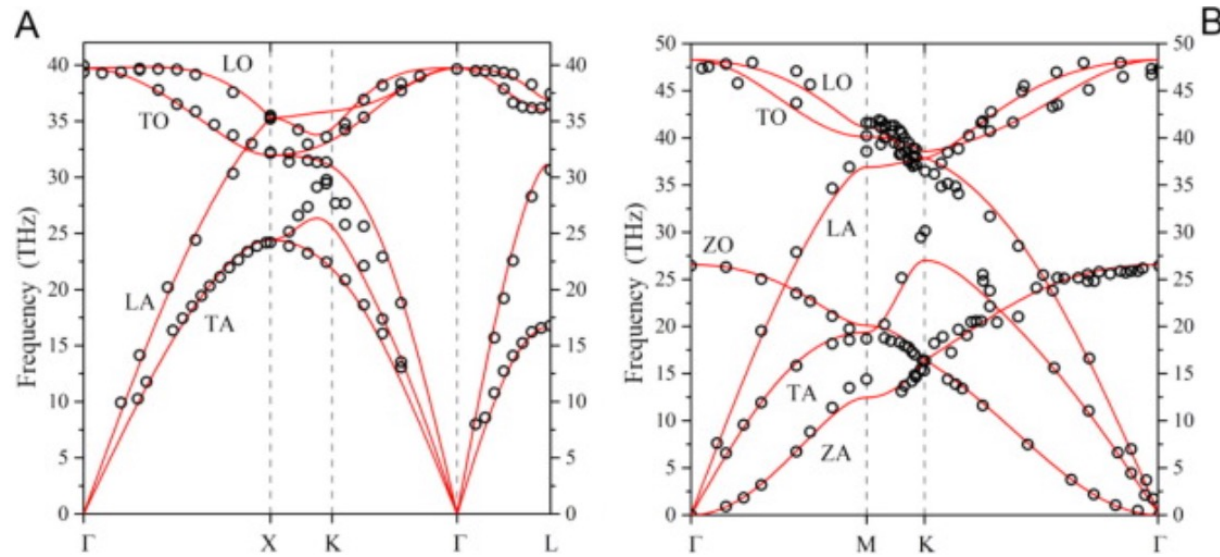
Within the MIT Atomic-Scale Modeling Toolkit we can use stand-alone XCrySDen.

A. Kokalj, *J. Mol. Graphics Modelling* 17, 176-179 (1999); <http://www.xcrysden.org/>

Try diamond.xsf, and consider:

- Which of the 3D Bravais lattices is this?
- Do we have a special name for this structure (lattice + basis)?
- Look at primitive and conventional cells, switching between them via Display menu.
- What are the lengths of each lattice vector?
- What is the angle between the lattice vectors?
- What is the basis? How many atoms in the unit cell?
- How many nearest neighbors does each atom have?
- Measure bond lengths and angles among nearest neighbors.
- Try out Display->Wigner-Seitz Cells.
- Rotate the structure in different directions and find special directions of viewing in which all the atoms look lined up; describe them as [100], [110], etc. with Miller notation.

Example of Brillouin zones and k-paths from literature: Phonons in 3D and 2D



U. Monteverde *et al.*, *Carbon* 91, 266-274 (2015)

diamond

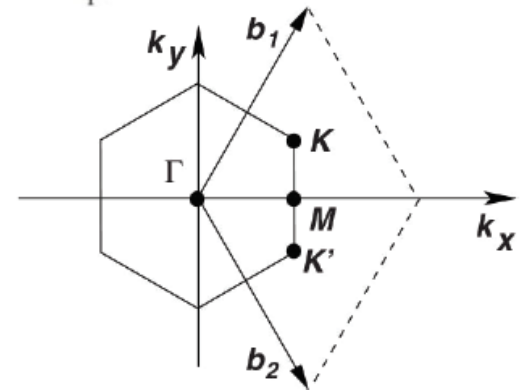
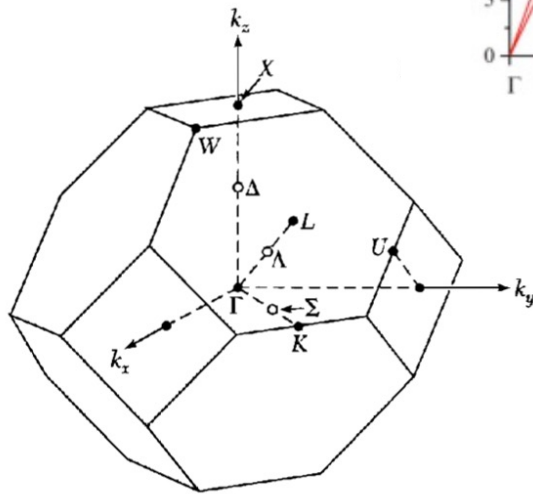
graphene

Branch labels:

L = longitudinal,

T = transverse,

Z = out-of-plane (just for 2D materials)



Exploring k-paths in Brillouin zone

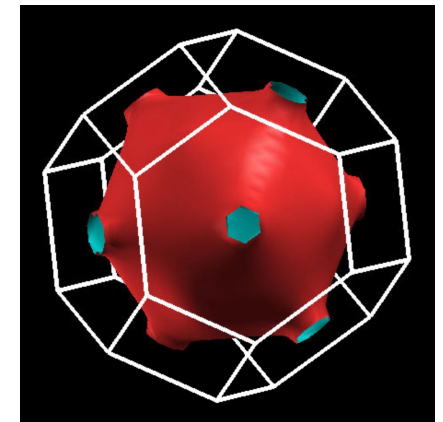
- Open the structure, and click Tools -> k-path Selection.
- Click “Close” at the bottom of the pink tab which appears, which probably says that it doesn’t know what kind of Bravais lattice you have.
- You see a wireframe model of the Brillouin zone of the crystal.
- The $k=0$ (Γ) point is marked in red.
- Other high-symmetry points are marked in black.
- Follow the tour through the BZ marked in the previous slide for diamond or graphene, using the diagram of the Brillouin zone to identify the location of the appropriate points. Note that there are many copies of some of the high-symmetry points: there is only one Γ , but every center of a square face is X, every center of a hexagonal face is L, etc. Choose the closest point bearing a given label at each step.
- Turn the BZ around to see how the k-path looks. Save a copy of it by screenshot.
- Note: the “Conventional Brillouin Zone” will be the same as the “Primitive Brillouin Zone” view, because you have to separately specify a set of conventional lattice vectors to get a different view, and we didn’t do that.

Visualizing Brillouin zones and Fermi surfaces in XCrySDen

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- Go to MIT Atomic-Scale Modeling Toolkit on nanoHUB.
- Select new subtool, “Crystalline Structures and Densities (XCrySDen)”
- Select File type: “BXSF file (.bxsf)”
- Under “File to open” there are several examples. Select Cu.bxsf (fcc), and click Simulate.
- In the tab that opens up, accept the default Fermi energy by clicking “ok”.
- In the next tab, tick the box next to each of the bands and click “Selected.”
- Now a tab opens up with a visualization of the Brillouin zone, shown as a polyhedron with white edges. Which band shows a colored surface, the Fermi surface? Only one band crosses the Fermi level in this case. Look at that band.
- Click the second-from-the-top button in the upper left, to convert to the parallelepiped reciprocal cell instead of the Brillouin Zone (BZ). Typically this view will not give a closed Fermi surface.
- Click the top button in the upper left to return to the BZ. This is the Wigner-Seitz cell in reciprocal space, the most compact cell.
- Click the third button down to see how the Fermi surfaces connect between BZs.

$$\left\{ \vec{k} \mid \epsilon_n(\vec{k}) = \epsilon_F \right\}$$



Visualizing Brillouin zones and Fermi surfaces in XCrySDen

- Rotate Brillouin zone around by clicking and dragging to get an idea of its shape.
- There are 7 boxes on the upper left side which offer different visualization options. If you hover the mouse over them, a description will pop up. Try “display solid cell” for a different view. Also try “display reciprocal cell”: how is that different from the Brillouin zone?
- What kind of polyhedron is this?
- How many faces are there, and what are their shapes?
- What is the real-space lattice of this crystal?
- What is the reciprocal-space lattice of this crystal, and how is it related to the real-space lattice?
- Try each of the different examples. In some cases, you will see no Fermi surface, because it is an insulator or semiconductor. Diamond and graphite may take a while to load.
- Compare the different fcc structures’ Brillouin zones.
- Compare hexagonal graphite and MgB_2 to each other and to MoS_2 3R.